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(19)



(54) PLASTISOL OF AN ORGANIC POLYMER AND A PLASTICISER

(71) We, TEROSON GMBH, a German Body Corporate, of Hans-bunte-
Strasse 4, 6900 Heidelberg 1, Germany, do hereby declare the invention for which we
pray that a patent may be granted to us, and the method by which it is to be performed,
to be particularly described in and by the following statement:—

5 The invention relates to novel plastisols containing acrylate polymers and organic
plasticisers.

10 Plastisols are generally understood to mean dispersions of organic plastics in
plasticisers, which are gelled on heating to an elevated temperature. Conventional
plastisols generally comprise pulverulent polyvinyl chloride dispersed in a compatible
liquid plasticiser which forms a paste. Polyvinyl chloride plastisols are used for
numerous different purposes, particularly as sealing compounds, as anti-corrosive
coatings for metals, for impregnating and coating textile substrates and as cable
insulations.

15 However, several serious problems occur in the production and use of PVC-
plastisols. In fact, the production of PVC itself represents a problem because persons
working in the production area may be exposed to a health risk by the vinyl chloride.
Of late this has led to the closing of a large number of PVC factories. Residual monomer
in the PVC could also endanger people during processing, and possibly even the final
consumer if the plastigel comes into contact with foodstuffs.

20 PVC-plastisols also suffer from the disadvantages in that PVC is both sensitive
to light and heat, and that there is a tendency to split of hydrogen chloride. The
splitting off of hydrogen chloride represents a particularly serious problem because
during use the plastisol must be heated to an elevated temperature. Any hydrogen
chloride liberated under these conditions has a corrosive effect and, for example,
corrodes metal substrates. Attempts have been made to counteract this thermal decom-
position by adding heat stabilisers, but these compounds are frequently toxic so that
they cannot be used where the plastisol comes into contact with foodstuffs. These
problems are further exacerbated when, in certain species cases, PVC-plastisols require
relatively high baking temperatures in order to obtain very short gelling times. In
these circumstances the danger of PVC-decomposition is further increased.

25 According to the present invention, there is provided a plastisol, comprising (a)
100 weight parts of solid particles of average size 0.1 to 500 microns of an organic
polymer consisting substantially of units derived from

30 (i) one or more of: t-butyl acrylate, a C_{1-4} alkyl methacrylate or cyclohexyl
methacrylate, or

35 (ii) one or more of the above monomers and one or more comonomers selected
from methacrylates of aliphatic C_2 to C_{10} alcohols, acrylates of aliphatic C_1-C_{10}
alcohols, styrene and alpha-methyl styrene, said polymer having a glass transition

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5 The plasticiser selected must of course be completely compatible with the particular acrylic polymer. A useful simple test of compatibility is that at least 8 days after the gelling of the plastisol, the plasticiser does not exude, as shown by a completely dry and non-tacky surface. Naturally, the compatibility is dependent both on the type of acrylic polymer and on the type of plasticiser. For example, dibutylphthalate is not a suitable plasticiser for polymethylmethacrylate because compatibility is inadequate. However, the same plasticiser can be used for copolymers of methylmethacrylate and approximately 5 to 25% of butyl methacrylate.

10 A further important criterion for selecting suitable plasticisers is the storage stability of the plastisol. This can be quantitatively defined by the viscosity index (based e.g. on a 1:1 polymer/plasticiser mixture) in the following manner:

$$V_{\%} = \frac{\eta_{8d}}{\eta_0}$$

15 wherein $V_{\%}$ represents the viscosity index $\eta_{\%}$ the initial viscosity of the plastisol, and η_{8d} the plastisol viscosity after standing for 8 days.

20 The viscosity is determined by means of conventional methods of determination, e.g. with a rotary viscosimeter (Drage). According to the definition indicated above the viscosity index of the plastisol of the present invention must be below 3.0, i.e. the viscosity may only rise a maximum of less than three times the initial viscosity of the plastisol within a period of 8 days. Such a plastisol would still not necessarily always be adequately stable, but this can easily be remedied, e.g. by increasing the plasticiser content or adding fillers or other additives.

25 The selection of the most appropriate plasticiser can again be explained with reference to the accompanying drawing. Within the triangle XYZ, which encloses the suitable acrylic polymers, there is a smaller triangle for each usable plasticiser within which are located those acrylic polymers which can be combined with a particular plasticiser to give a usable plastisol. The zones for the individual plasticisers are limited to the left by the compatibility with the polymer, and upwards (hypotenuse of the triangle) by the viscosity index (storage stability). For each plasticiser these limits can be determined by simple experiments. As examples, the drawings show the zones GYH, 30 DEF and ABC for dimethoxy-ethylphthalate (DMEP), dibutylphthalate (DBP) and diethylphthalate (DOP).

35 Plasticisers having at least two aromatic rings and/or two ether groups in the molecule have proved particularly suitable for polymethyl methacrylate. The first group includes, for example, butylbenzyl phthalate, dibenzyl toluene, dibenzyl phthalate, diphenyloctyl phosphate, triphenyl phosphate, tricresyl phosphate, dibenzyl benzoate, and diphenylether. The second group includes, among others, dimethoxy-ethyl phthalate, diethoxyethyl phthalate, dibutoxyethyl phthalate and methylphthalylethyl glycolate. Both criteria are satisfied by diethyleneglycol dibenzoate and dipropylene glycol dibenzoate. A further preferred plasticiser is acetyl tributyl citrate.

40 When methacrylic copolymers are used, generally the compatibility with plasticisers increases, but in many cases there is a viscosity index of at least 3.0, i.e. an inadequate stability. For example, for a copolymer of 15% n-butyl-methacrylate and 85% methyl methacrylate with an average particle size of 100 μm , dibutyl phthalate, diisobutyl phthalate and diamyl phthalate are also suitable in addition to the above-indicated plasticisers. However, if in the case of these polymers the particle size is reduced to 2 μm , the viscosity index for most of the indicated plasticisers rises to at least 3.0. However, tricresyl phosphate and dibenzyl toluene still remain suitable as plasticisers.

45 Conventional plasticisers such as diethyl phthalate, dinonyl phthalate and others require a still higher comonomer content in the copolymer in order to obtain an adequate compatibility.

50 In the case of a copolymer consisting of 50 parts by weight of butyl methacrylate and 50 parts by weight of methyl methacrylate and having an average particle size of 50 μm , even if the necessary compatibility exists, it is impossible to obtain an adequate storage stability with most of the above-indicated plasticisers. However, diethyl phthalate, dinonyl phthalate, didecyl phthalate, butyl cyclohexyl phthalate and the like remain suitable as plasticisers in such cases. Thus, with an increasing comonomer content in the polymer, the aliphatic groups in the phthalate may proportionally become longer. While pure aliphatic plasticisers such as adipates or sebacates are unsuitable it is then possible to use higher boiling aromatic, hydrocarbons with aliphatic groups. For example, Ingralur 839 (hydrocarbon mixture containing more than 40% aromatics, produced by the Fuchs Company, Mannheim) has proved suitable for the

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temperature of above 35°C and an average degree of polymerisation of more than 400, and (b) 30 to 1000 weight parts of an organic liquid component which serves as a compatible plasticiser for the organic polymer, to form a viscous dispersion having a liquid or paste-like appearance and a viscosity index V_{10} (as hereinafter defined) of less than 3.0.

These plastisols possess the excellent processing and product qualities of PVC-plastisols, but gel at lower temperatures and are also chlorine-free so that there can be no splitting off of the chlorine or hydrogen chloride. The average particle size of the polymer used is preferably increased proportionally with the decrease of its glass transition temperature T_g . The glass transition temperature is preferably above 60°C.

To obtain usable results, the degree of polymerisation of the polymer used must be at least 400. Advantageously the degree of polymerisation is between 400 and 20,000, corresponding to an average molecular weight of about 40,000 to 2,000,000.

The preferred polymer component consists substantially wholly of one kind of units derived from t-butyl acrylate, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl or t-butyl methacrylate or cyclohexyl methacrylate, i.e. is essentially a homopolymer. Methyl methacrylate is preferred. The alcohol acrylate or methacrylate comonomers preferably have an alkanol alcohol component, i.e. are unsubstituted and saturated, and the type (i) monomers, i.e. those listed above, will generally predominate over those of type (ii). The preferred copolymers are those in which one of the monomers is methyl methacrylate and constitutes at least 40%, preferably at least 50%, by weight of the total monomer units, and the other component is a C_{1-4} alkyl methacrylate, especially n-butyl methacrylate, or a C_{1-4} alkyl acrylate.

However, only those copolymers whose glass transition or solidification temperature is above 35°C can be employed in the plastisols of the present invention. The glass transition temperature T_g of a particular copolymer can be calculated beforehand by the Fox formula (T. G. Fox, Bull. Am. Phys. Soc., vol. 1, 123 (1956)):

$$\frac{1}{T_g} = \frac{W_1}{T_{10}} + \frac{W_2}{T_1} + \dots + \frac{W_n}{T_n}$$

wherein W_1 represents the weight portion of monomer 1, W_2 the weight portion of monomer 2, T_1 the glass transition temperature of the polymerised monomer 1 in °K, T_2 the glass transition temperature of the polymerised monomer 2 in °K, T_{10} the glass transition temperature of the copolymer in °K.

The average particle size of the polymer used must be from 0.1 μm to 500 μm , preferably from 0.3 to 200 μm . If too large a particle size is used, the plastisol obtained will not have an adequate internal bond, and no complete gelling of the polymer occurs. If the particle size is too small, the storage stability is inadequate, i.e. gelling occurs even when the polymer is left to stand.

The accompanying drawing is a graph in which the logarithm of the average particle size (in μm) of the organic polymer (a) has been plotted against the glass transition temperature T_g (in °C) of this polymer. There is an interdependence between the average particle size of the polymer (a) and its glass transition temperature T_g such that the polymers most suitable for the plastisols according to the invention substantially occur within the triangle XYZ formed by the coordinates (minimum glass transition temperature, \log [maximum average particle size]), (105°C, \log [maximum average particle size]) and (105°C, \log [minimum average particle size]). It can also be seen that the higher the glass transition temperature of the polymer, the lower can be its average particle size. However, extremely fine-grained polymers with a low glass transition temperature are not suitable.

It is also within the scope of the present invention to use two polymers having different average particle sizes. As a result of using a mixture of a fine-grained and a coarse-grained polymer, it is possible to control with certain limits the flow characteristics and plasticiser requirements (cf. e.g. German Patent Specification No. 934,498).

Both suspension-polymerized and emulsion-polymerized acrylic polymers are suitable for the plastisols according to the invention. In the case of suspension-polymerisation, the desired particle size can be controlled by the stirring rate, and in the case of emulsion-polymerisation by the quantity and type of emulsifier. The particle size of the polymer is determined in conventional manner, e.g. by means of a Coulter counter.

Preferably 65 to 800 parts by weight of plasticiser are used per 100 parts by weight of polymer.

latter copolymers. In the case of a comonomer content of 70% butyl methacrylate very coarse particles are required, but phthalates cannot be used due to the too limited storage stability. However, plasticisers such as Ingralur 839, polymerol (naphthenic hydrocarbons produced by Shell) and tri-(ethylhexyl)-mellitate and high-boiling aromatic oils remain suitable.

Many plasticisers which have a good storage stability but poor compatibility with particular polymers, making them unsuitable *per se* for plastisol formation, can, in certain circumstances, be used as so-called extenders to replace up to 25% by weight of the main plasticiser. These extenders particularly include plasticisers which are alone only compatible in the case of a high comonomer content.

Finally, it is also possible to use so-called polymer plasticisers if they are compatible with the particular acrylic polymer used. In this connection the plastisol viscosity is substantially dependent on the viscosity of the polymer plasticiser, which is always significantly higher than that of the monomeric plasticisers. Suitable polymer plasticisers are e.g. ortho- and para-phthalate-based polyesters.

If different plasticisers can be used for the compounding of a plastisol from a specific acrylic polymer or co-polymer, the choice will ultimately depend on the end use of the plastisol. Thus, polymethyl methacrylate can advantageously be used together with acetyl tributyl citrate for food applications (container gaskets) while other technically feasible plasticisers would not be suitable for this purpose.

In addition to acrylic polymers and plasticisers, the plasisols according to the invention can contain up to 700, preferably up to 400 parts by weight of inert fillers per 100 parts by weight of polymer. The fillers mainly serve to increase the viscosity as well as to improve the abrasion resistance. They also permit a cost saving. Suitable fillers are chalks which can, e.g. be ground, precipitated or coated. Barite, kaolin, highly dispersed silica, talc, bentonite, glass powder, sand, aluminium oxide and hydroxide, antimony trioxide, titanium dioxide, carbon black, metal soaps, such as zinc or calcium stearate, dyes, pigments and corrosion inhibitors may also be added to the plasisols.

In addition, the plasisols can contain conventional additives, for example viscosity regulators such as emulsifiers and silicones, further oxidation, light and heat stabilisers, as well as epoxide softeners. It is also possible to add foaming agents, for example azo-compounds which decompose during gelling and lead to a foamed plastigel.

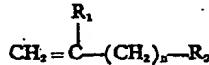
It is finally particularly important to ensure the adhesion of the plasisols according to the invention on the particular substrate to be treated, e.g. steel (greased, degreased, phosphatised, primed) aluminium, textiles, papers and others. Suitable adhesion promoters for this purpose are, for example, triethylenglycol dimethacrylate or trimethylol trimethacrylate, in combination with peroxides which decompose at the gelling temperature, and initiate a radical polymerisation of the adhesive.

Liquid or solid phenol or resorcinol resins with a low formaldehyde content are also suitable. It is also possible to use epoxide resins with heat-reacting hardeners such as acetoquanamine or dicyano-diamide, as well as amino-silanes. The adhesion promoter content can be present in an amount of from 0.1 to 50, preferably from 1 to 5, parts by weight, to 100 parts by weight of polymer.

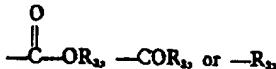
The adhesion can also be improved by co-polymerising a small quantity (based on the polymer and/or copolymer) of the acrylic or methacrylic monomer(s) of the polymer (a) with an acrylate or methacrylate monomer with free functional groups. The proportion of such comonomers is generally up to 3% by weight of the resulting polymer (a). Acrylate and/or methacrylate monomers with free carboxyl, hydroxy, epoxy or amino groups are particularly suitable. In particular, it is possible to use free acrylic acid or methacrylic acid, or esters thereof with lower aliphatic oxy, epoxy or amino alcohols.

Alternatively, adhesion can be improved by copolymerising monomer(s) of the polymer (a) with from 0.1 to 3%, more preferably from 0.2 to 3%, by weight (based on the polymer and/or copolymer or monomer/s to be polymerised) of one or more copolymerisable monomers having a heterocyclic group with at least one nitrogen atom in the ring. Excellent results have been obtained with amounts of the copolymerisable heterocyclic compound in this range. Optionally, however, the proportion of the heterocyclic compound(s) can be increased, e.g. to up to 5%, and in special cases even up to 10%, by weight.

Preferably, a heterocyclic vinyl compound of the general formula



is used as a comonomer for the co-polymerisation, in which n is 0 or 1, R₁ is a hydrogen atom, a linear or branched alkyl group of from 1 to 4 carbon atoms or a phenyl group and R₂ is a group of the formula



5 in which R₃ is a heterocyclic group having one or several rings with at least one nitrogen atom in the ring. 5

Suitable monomers are, for example N- or C-vinyl or N- or C-allyl compounds of imidazole, imidazoline, imidazolidine, benzimidazole, triazole, pyrrole, pyrazole, 10 oxyazole, pyridine, chinoline, diazine as well as other heterocyclic compounds with at least one nitrogen atom in the ring system, N-vinyl imidazole is particularly preferred. Furthermore, vinyl and allyl ethers and acrylic or methacrylic acid esters of the heterocyclic compounds are useful. 10

15 The adhesion of the plastisols can be further improved by adding additional cross-linking agents which react with the heterocyclic group of the co-polymerised monomer. Preferably the plastisol contains the cross-linking agent in an amount of from 0.1 to 3.0% by weight. Epoxy resins were found suitable; apart from the commercial epoxy resins a polymer can also be used which, according to the present invention has been co-polymerized with a small amount of acrylate and/or methacrylate monomer with epoxy groups. Furthermore, polybasic carboxylic acids, e.g. benzene tricarboxylic acid, adipic acid, maleic acid and itaconic acid, have proved to be suitable, either as the 20 only cross-linking agent present or together with a polyepoxide, to effect a further improvement of the adhesion properties. 20

25 Preparation of the plastisols according to the present invention can also be effected by blending together two or more acrylate or methacrylate polymers which meet the requirements of the invention. For example, a methyl methacrylate homopolymer can be blended with a methyl methacrylate copolymer or with a copolymer which has been further modified by co-polymerisation with a heterocyclic compound. In this manner, particularly favourable rheological properties can be obtained. 25

30 It is also possible to blend copolymers containing groups which react with each other. The above-described combination of copolymers with epoxy groups and of copolymers with heterocyclic groups is one example for this method. 30

35 The plastisols according to the invention can be processed in conventional manner dependent on the particular viscosity, for example by applying with a float, coating with a brush, applying with a paint gun, spraying with an atomiser and air, spraying by high pressure (without air), scraping on, calendering, pouring or immersing. 35

40 Finally, to form the plastigel the plastisols must be gelled. For this purpose temperatures between about 70 and 240°C are used, dependent on the plastisol composition and the particular working conditions. The necessary gelling time is between two minutes and two hours. The necessary heating can take place, for example, by hot air, metal pipes, infra-red rays, high frequency heating, etc. 40

45 The plastisols according to the invention can be shaped and gelled to form shaped plastics articles. The plastisols are particularly suitable as abrasion and corrosion inhibitors for steel sheets, for example as underbody-protection for automobiles, trucks and buses. The plastisols can also be used for seam seals for levelling out folding systems, as metal adhesives, coating compounds, spot welding compounds, expanding pastes, sealing agents for spot welded sheets and for sealing double-danged seams. They can also be used for impregnating and coating textiles and similar substrates such as tarpaulins, artificial leather, floor coverings, carpet backings, packaging materials, conveyor belts and driving belts. Using the immersion process, it is possible 50 to produce hollow bodies, gloves, boots, finger stalls etc. The plastisols may also be shaped and gelled to form sealing gaskets, such as seals for bottle caps and folding seams, as plastic seals for air and oil filters, for extrusion and injection moulding highly elastic sections and items such as sealing strips and packaging cords, trays, technical components and for rolling foils and strips. If appropriate plasticisers and additives are used, the plastisols according to the invention are also suitable for packaging food-stuffs because there are no objections to methyl methacrylate. 50

55 The following Examples 3, 4, 6, 8, 10, 15 to 20 and 25 to 34 illustrate the present invention. Examples 1, 2, 5, 7, 9, 11 to 14, and 21 to 24 are comparative. All formulations are given in parts by weight unless otherwise stated.

60 Examples 1 to 15. 60
Table 1 gives the results of 15 Examples. In Examples 1, 2, 7, 11 and 12 the

plasticiser used was unsuitable for the particular polymer due to inadequate compatibility. In Examples 5, 9, 13 and 14 the value of 3.0 for the viscosity number was exceeded when using the indicated plasticiser, so that these combinations are also unsuitable. However, excellent results were obtained with the polymer/plasticiser combinations of Examples 3, 4, 6, 8, 10 and 15, wherein the plasticiser satisfied was both completely compatible with the polymer and the viscosity index V_{40}/V_{20} of the resulting plastisol was less than 3.0.

TABLE 1

Example	Parts by weight of polymer	T_g in °C	Particle diameter in μm	Parts by weight of plasticiser	Viscosity in CP			V_{40}/V_{20}	Elasticity
					Compatibility	immediately	after 8 days		
1	50 PMMA	105	30	50 DOP	bad	910	990	1.09	good
2	"	"	"	50 DIBP	moderate	720	1180	1.64	good
3	"	"	"	50 TKP	good	2630	3070	1.17	very good
4	"	"	"	50 DPGB	good	3450	3770	1.01	very good
5	50 MMA/ BMA 85/15	89	2	50 DIBP	good	2900	solid	∞	good
6	"	"	"	50 TKP	good	9050	21000	2.32	very good
7	"	"	"	50 DOP	moderate	4850	7300	1.51	good
8	"	"	"	50 DBT	good	2870	6850	2.39	very good
9	50 MMA/ BMA 50/50	56	50	50 DIBP	good	8200	solid	∞	very good
10	"	"	"	50 DOP	good	15900	35000	2.20	very good
11	"	"	"	50 DOA	moderate	1150	2400	2.09	good
12	"	"	"	50 TEHM	moderate	13600	13400	0.98	hard, elastic
13	50 MMA/ BMA 30/70	40	240	50 DIBP	good	5250	solid	∞	soft, tacky
14	"	"	"	50 DOP	good	32750	solid	∞	very good
15	"	"	"	50 TEHM	good	18100	14000	0.77	good

BMA — n-butylmethacrylate
DOP — dioctyl phthalate
PMMA — polymethyl methacrylate
DIBP — diisobutyl phthalate
TKP — triethylhexyl phosphate

DPGB — dipropylene glycoldibenzate
DBT — dibenzyl toluene
DOA — dioctyl adipate
TEHM — triethylhexyl malonate
MMA — Methyl methacrylate

Example 16.

The following mixture is homogenised with a stirrer and applied with a doctor blade to a degreased steel sheet:

5 30 parts PMMA (30 μm)
 30 parts butylbenzyl phthalate
 36 parts chalk
 3 parts triethylenglycol dimethacrylate
 0.3 parts tert.-butylperbenzoate

10 If this mixture is gelled for 20 minutes at 170°C, a tough strongly adhering film is obtained which has good anti-corrosive properties.

Example 17.

30 parts copolymer (MMA/BMA 50/50) (50 μm)
 30 parts dinonyl phthalate
 40 parts chalk

15 5 parts resorcinol resin (Rousselot RH 74-01)
 This mixture was tested as a metal adhesive by gelling it at 170°C between two metal plates of (a) steel and (b) aluminium. The subsequent tearing revealed a tensile strength of (a) 52 kg/cm² and (b) 42 kg/cm² (5 cm² bonding area and 0.3 mm coating thickness). However, if in place of the 50 μm copolymer, a copolymer with an average particle size of 500 μm is used, a tearing value of only 3 kg/cm² is obtained.

Example 18.

25 24 parts MMA/BMA 85/15 (2 μm)
 33 parts dibenzyl toluene
 40 parts chalk
 3 parts azodicarbonamide
 This mixture gelled in 15 minutes at 170°C and formed a highly elastic solid foam with 100% foam expansion.

Example 19.

30 20 parts PMMA (particle size 30 μm)
 30 parts butylbenzyl phthalate
 45 parts chalk
 5 parts resorcinol resin (Rousselot RH 74-01)
 This highly viscous substance was suitable as a sealing compound for metal welding seams in the automobile and refrigerator industry. After baking at 180°C for 15 minutes the substance adhered well to polished metal sheets and can be easily lacquered.

Example 20.

40 If a polymer plasticiser (a liquid urea/formaldehyde plasticiser resin sold as Plastigen) is used the following comparison is obtained with a polymer:plasticiser mixing ratio of 1:1.

TABLE 2

Polymer	Particle size μm	Viscosity in cP			Compatibility	Elasticity
		immediately	after 8 days			
100% PMMA	30	22000	16000	good	hard	
MMA/BMA 85/15	2	163000	218000	good	hard, tough	
MMA/BMA 50/50	60	23250	22250	good	elastic	

Example 21 (comparison).
Table 3 shows the thermal stability of an acrylic plastisol as compared with a PVC-plastisol with a baking cycle of 30 minutes at 150°C.

TABLE 3

		1	2
Emulsion PVC, K-value 74 (2 μ m)		20	
PMMA (30 μ m)			20
Chalk		45	45
Butylbenzylphthalate		35	35
Viscosity in cP	immediately after 10 days	36000 21000	52500 18000
	$V_{10/0}$	0.58	0.34
Cold elasticity	-40°C	++	++
Discolouration after 14 days at	120°C 150°C	slight black	slight slight
Abrasion (mm/min) after 14 days storage at	amb. temp. 120°C 150°C	0.016 0.039 1.280	0.045 0.390 0.220

5 The Table shows that after 14 days at 150°C the PVC-plastisol had completely discoloured (decomposed) and that the abrasion values in a sand-blasting device (with corundum in place of sand) rose 80 times in the case of PVC, whereas in the case of the acrylic plastisol the abrasion values, although not originally especially good, only rose by a maximum of 5 times. 5

10 Example 22 (comparison).

On comparing the following mixtures:
25 parts PVC (paste type, emulsion-polymerised, K value 74, 2 μ m)
40 parts chalk
5 parts iron oxide (magn.)
15 27 parts DOP
3 parts triethyleneglycol dimethacrylate
0.3 parts tert-butylperbenzoate
and the same mixture with

20 25 parts copolymer MMA/BMA 50/50 (50 μ m particle diameter)
in place of PVC by coating them between two overlapping steel sheets and then joining the two sheets by spot welding, in the case of the PVC decomposition and hydrogen chloride formation occurs, whilst when left standing in air there is pronounced corrosion at the points where PVC-decomposition took place. This was not observed in the case of the methacrylate plastisol. 20

25 Example 23 (comparison).

a) 60 parts PVC (as in Example 22)
40 parts DOP
b) 60 parts PVC (as in Example 22)
40 parts DBP
c) 60 parts MMA/BMA 50/50 (50 μ m)
40 parts DOP
d) 60 parts PMMA (30 μ m)
40 parts DBP
35 for 10 minutes at 200°C they gelled to form a transparent film, but the PVC is always discoloured yellow to brown, whereas the acrylic resin remains colourless. 35

On gelling together the following components.

a) 30 parts PVC (as in Example 22)
 30 parts DOP
 20 parts chalk
 5
 20 parts barite
 b) 30 parts MMA/BMA 85/15 (2 μm) in place of PVC otherwise as a)
 for 30 minutes at 70°C, in the case of a) a crumbly substance is obtained and in the case of b) a solid tough film.

10 Examples 25 to 28.
 For the preparation of the following plastics in each case a copolymer was used which was polymerised with 1% by weight of a methacrylate monomer with a functional group. The plastics obtained in this manner were tested for their adhesion properties using the method described in Example 17. The results compiled in the attached Table 4 show that excellent adhesion values were obtained.

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TABLE 4

Example	Parts by weight Polymer	Parts by weight Plasticizer	Parts by weight Filler	Bonding Strength in kg/cm ²	Substrate	Polymer Particle size in microns
25	50 MMA/BMA/ methacrylic acid (84: 15: 1)	50 DBT		25	degreased metal sheet	10
26	20 MMA/BMA/ methacrylic acid (84: 15: 1)	45 DBT	35 chalk	4.2	primed metal sheet	10
27	50 MMA/BMA/ glycidyl methacrylate acrylate (84: 15: 1)	50 DBT			untreated metal sheet	5
28	50 MMA/BMA/ dimethyl amino ethyl methacrylate (84: 15: 1)	50 DBT		7.2	Smoothened Metal sheet	10
				Film cannot be removed		

Example 29.

(a) A plastisol was prepared from 50 parts by weight of a copolymer from methylmethacrylate and n-butylmethacrylate (MMA/BMA 85:15; particle size approximately 2 μm) and 50 parts of dibenzyl toluene.

5 This plastisol was tested as metal-to-metal adhesive by applying it to two degreased metal sheets (bonding area 5 cm^2 and 0.3 mm layer thickness) and gelling it for 30 minutes at 180°C. The subsequent tear-off test (tearing speed: 100 mm per minute) did not yield a bonding strength value.

10 (b) The test was repeated using 50 parts by weight of a terpolymer which was copolymerised with 1 part by weight of N-vinyl imidazole (MMA/BMA/vinyl imidazole 84:15:1). Under otherwise unaltered conditions a bonding strength value of 13 kg/cm^2 was now obtained.

15 When the above plastisol, with a content of N-vinyl imidazole, according to the invention was used for the bonding of test sheets which had been electro-coated with a dip primer as it is used in the automotive industry a bonding strength value of 28 kg/cm^2 was obtained.

Example 30.

20 A further plastisol was prepared from 20 parts by weight of copolymer (MMA/BMA/N-vinyl imidazole 84:15:1) of particle size 10 microns, 35 parts by weight of chalk and 45 parts by weight of dibenzyl toluene. Upon gelling for 30 minutes at 180°C on an EC primed metal sheet a bonding strength value of 11 kg/cm^2 was obtained.

25 The same plastisol surprisingly yielded bonding strength values of 14 to 12 kg/cm^2 , respectively, when applied to degreased or slightly greasy metal sheets.

If, for comparative purposes, a methyl methacrylate homopolymer or a methyl methacrylate/butyl methacrylate copolymer is used which was not copolymerised with an adhesion promoter, no bonding strength value was obtained.

Example 31.

30 A plastisol was prepared from 50 parts by weight of a copolymer (MMA/N-vinyl imidazole 99:1) of particle size 20 microns, 30 parts by weight of chalk and 45 parts by weight of butylbenzyl phthalate. Upon gelling for 30 minutes at 90°C the plastisol coating on the primed metal sheet could not be removed.

If, however, the imidazole group is left out of the polymer no adhesion is obtained.

Example 32.

35 Following Example 29 (b) a plastisol was prepared to which 1% by weight of one of the polybasic carboxylic acids listed below was added. The results show that the adhesion was considerably improved.

TABLE 5
Bonding Strength Values in kg/cm^2
after Gelling for 30 Minutes at

Acid	120°	160°
None	11.5	20.0
Benzene tricarboxylic acid	20.2	28.0
Adipic acid	22.3	19.6
Maleic acid	34.2	30.7
Itaconic acid	27.8	25.3

Example 33.

40 A plastisol was prepared from the following ingredients:
100 parts poly(methyl methacrylate), of 35 microns particle size
85 parts acetyl tributyl citrate
5 parts titanium dioxide
5 parts zinc stearate

The plastisol thus prepared was lined into the peripheral annular channel of lug caps by means of conventional lining machinery and the lined material was fluxed for one minute at 350°F (177°C).

5 The resulting gasketed lug caps were tested for sealing ability by determining their vacuum retention performance with the following procedure: A jar is filled with boiling water to one half inch from its top. A lug cap is sealed on with 35 inch pound (0.40 mkg) torque. The resulting assembly is cooled to room temperature and kept for one week. A vacuum reading is then obtained by means of a vacuum gauge. After removal of the cap, the compressed gasket thickness is measured.

10 All jars tested with lug caps gasketed with the above composition held a vacuum satisfactorily. Gasket thicknesses ranging from 20 to 35 mils (0.5 to 0.9 mm) were acceptable.

Example 34.

A plastisol was prepared with the following ingredients:

15 100 parts poly(methyl methacrylate), of 35 microns particle size 15
120 parts acetyl tributyl citrate
5 parts titanium dioxide
5 parts zinc stearate
4 parts azobisisformamide

20 1.5 parts Lightweight silica (Cab-O-Sil) 20
This composition was lined into a wide-mouth jar closure (83 mm diameter) by conventional means. The lining was fluxed for 1.5 minute at 350°F (177°C).

25 The caps thus obtained were applied to jars with a 32 inch pound (0.36 mkg) torque and kept at room temperature for 24 hours. They were then placed on a stacker for one week, being subjected in the process to a net load of 128 lbs (57 kg) on each cap and jar assembly. The jars were then removed, kept at room temperature for 24 hours and placed in a cold room for two days. Vacuum was determined at 40°F (4°C) by means of a gauge. Nine out of ten jars tested held 40 mmHg, an acceptable performance.

30 WHAT WE CLAIM IS:—

1. A plastisol comprising (a) 100 weight parts of solid particles of average size 0.1 to 500 microns of an organic polymer consisting substantially of units derived from

35 (i) one or more of: t-butyl acrylate, a C_{1-4} alkyl methacrylate or cyclohexyl methacrylate, or 35
(ii) one or more of the above monomers and one or more comonomers selected from methacrylates of aliphatic C_6 to C_{10} alcohols, acrylates of aliphatic C_1-C_{14} alcohols, styrene and alpha-methyl styrene, said polymer having a glass transition temperature of about 35°C and an average degree of polymerisation of more than 400, and (b) 30 to 1000 weight parts of an organic liquid component which serves as a compatible plasticiser for the organic polymer, to form a viscous dispersion having a liquid or paste-like appearance and a viscosity index V_{50} (as hereinbefore defined) of less than 3.0. 40

45 2. A plastisol according to claim 1, wherein the organic polymer (a) consists substantially of units derived from methyl methacrylate or methyl methacrylate and a comonomer as defined in claim 1. 45

3. A plastisol according to claim 2, wherein the organic polymer (a) consists substantially of units derived from at least 40% by weight of methyl methacrylate and substantially all the balance being a C_{1-4} alkyl methacrylate or a C_{1-4} alkyl acrylate. 50

4. A plastisol according to claim 3 wherein the organic polymer (a) contains at least 50% by weight of methyl methacrylate. 50

5. A plastisol according to claim 1, wherein the organic polymer consists substantially of units derived from one of:— t-butyl acrylate, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, t-butyl, or cyclohexyl methacrylate, or from one of these monomers and a comonomer as defined in claim 1. 55

6. A plastisol according to any one of claims 1 to 5 wherein the average particle size of the polymer is related to its glass transition temperature so as to lie within the triangle XYZ of the accompanying drawing.

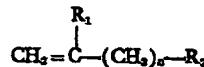
7. A plastisol according to claim 6 wherein the plasticiser is dioctyl phthalate, dibutyl phthalate or di(2-methoxyethyl) phthalate and the average particle size of the polymer is related to its glass transition temperature so as to lie within the triangle ABC, DEF or GYH, respectively, of the accompanying drawing. 60

8. A plastisol according to any one of claims 1 to 7 wherein the organic polymer (a) contains also up to 3% by weight, based on the polymer, of units derived from an acrylic and/or methacrylate monomer having a hydroxyl, epoxy, amino or free carboxyl group.

5 9. A plastisol according to any one of claims 1 to 7 wherein the organic polymer (a) contains up to 10% by weight of units derived from one or more comonomers containing a heterocyclic group having at least one nitrogen atom in a heterocyclic ring.

10 10. A plastisol according to claim 9 wherein the proportion of heterocyclic group-containing comonomer is from 0.2 to 3.0% by weight.

11. A plastisol according to claim 9 or 10 wherein the heterocyclic group-containing comonomer is a heterocyclic vinyl compound of the general formula



in which n is 0 or 1, R₁ is a hydrogen atom, a linear or branched alkyl group of from 1 to 4 carbon atoms or a phenyl group, and R₂ is a group of the formula:

15
$$\begin{array}{c} O \\ || \\ C-OR_3-COR_3 \text{ or } -R_3 \end{array}$$
 15

in which R₃ is a heterocyclic group having one or more rings, at least one nitrogen atom being present in at least one ring.

12. A plastisol according to any one of claims 9 to 11, which also contains a cross-linking agent in an amount of from 0.1 to 3.0% by weight which is capable of reacting with the heterocyclic groups of said comonomer.

20 13. A plastisol according to claim 12, wherein the cross-linking agent is a poly-epoxide and/or a polybasic carboxylic acid.

14. A plastisol according to any one of claims 1 to 13 which also contains from 0.1 to 50 parts by weight of an adhesion promoter.

25 15. A plastisol according to any one of the preceding claims which contains also up to 700 weight parts of inert filler.

16. A plastisol according to claim 2 substantially as described in any one of Examples 3, 4, 6, 8, 10, 15, 16, 17, 18, 19 or 20.

30 17. A plastisol according to claim 5 substantially as described in any one of Examples 29 to 32.

18. A plastisol according to claim 1 substantially as described in any one of Examples 25 to 28, 33 or 34.

35 19. Shaped plastics articles made by shaping and gelling a plastisol according to any one of claims 1, 3, 4, 6 to 15 or 18.

20. Shaped plastics articles made by shaping and gelling a plastisol according to claim 2 or 16.

35 21. Shaped plastics articles made by shaping and gelling a plastisol according to claim 5 or 17.

22. A sealing gasket produced by shaping and gelling a plastisol according to any one of claims 1, 3, 4, 6 to 15 or 18.

40 23. A sealing gasket produced by shaping and gelling a plastisol according to claim 2 or 16.

24. A sealing gasket produced by shaping and gelling a plastisol according to claim 5 or 17.

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